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Is it possible to increase the oil yield of catalytic pyrolysis of biomass? A study using commercially-available acid and basic catalysts in ex-situ and in-situ modus

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ABSTRACT

Catalytic pyrolysis of woody biomass and cellulosic materials has been investigated by analyzing the effect of catalysts on aqueous phase (sugar rich) and oil phase (lignin rich) organics produced by the preceding thermal pyrolysis. Tests were done in a downer reactor using ZSM-5 and Na_2O/γ-Al_2O_3 as typical commercially available catalysts. Both catalysts converted the aqueous phase organics to coke, water and gas, and deoxygenated and cracked the oil phase organics. The maximum yield of oil phase organics when applying the catalysts never exceeded the corresponding oil yield of thermal pyrolysis (~22% on carbon basis). Analysis of new results of ex-situ with in-situ catalysis, in combination with earlier reported data, indicates that a path forward to obtain higher oil yields is not expected to come from process improvements. The development of catalysts that can convert the aqueous phase organics (potentially ~35% on carbon basis) into organic phase ones, instead of cracking and polymerizing them to respectively gas and char, should be considered.

1. Introduction

Catalytic pyrolysis has been advocated to yield better quality liquids as compared to its thermal counterpart. [1–5] Research has been focusing on the production of chemicals such as aromatics [6–10], and partially deoxygenated pyrolysis oil as precursors for biofuels [4,11–15]. This paper deals with the production of biofuels via catalytic pyrolysis. Reported yields of catalytic pyrolysis oils for fuel application are low, between 14 and 26% on carbon basis [4,5,11,12,15] and the level of deoxygenation is limited to final oxygen concentrations of 15–20% by weight [5,11,16]. Obviously, improving these performance indicators would increase the potential of catalytic pyrolysis. In this account, an experimental study is reported that aimed at identifying the phenomena leading to the current low yields of catalytic pyrolysis which can serve as a basis to hypothesize on how the technology could advance. There is already a large amount of information available, though fragmented over studies on either catalyst or reactor type. [17–20] We present a systematic study in which two typical commercially available catalysts, one basic and acidic, are applied in two often studied operating modi, viz. in-situ and ex-situ catalysis.

1.1. Research approach

When the water content is higher than ca. 30% by weight, pyrolysis oil splits in two fractions, [21,22] viz. an oil phase and an aqueous phase. Our research approach makes use of the fact that the organics in the oil phase are clearly different from those in the aqueous phase. There is consensus that, in case of thermal pyrolysis, the aqueous phase is mostly composed of light oxygenates (e.g. acetic acid), monophenols (e.g. guaiacol), and sugars (e.g. levoglucosan), while the oil phase is mainly composed of lignin-derived oligomers (e.g. phenolics) [23–28]. Generalizing: aqueous phase organics (APO) are mostly sugar derived molecules with an oxygen content of ca. 50% and a mass averaged molecular weight (MMW) of 150 Da, whereas oil phase organics (OPO) are mostly of lignin origin with a lower oxygen content of 30% and higher MMW of 700 Da. We chose two commercial catalysts with a very different acidity, to cover the broad pallet of postulated reactions. We are aware of novel catalyst formulations that mainly aim at improving the yield of target compounds for chemicals production [29,30]. However, further development and scaling up of these catalysts will still require time and money, which may considerably impact to the process

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economy at this stage. In our attempt to create further knowledge of catalytic pyrolysis we have tracked what happens to the OPO and APO when adding those catalysts, at different catalysts to biomass ratios, to the pyrolysis process. The yields and composition of the OPO and APO of thermal pyrolysis experiments after forced phase separation by water addition were compared with the results of catalytic experiments that all produced naturally an oil and aqueous phase. Pine wood and cellulosic materials were used as feedstock. Thermal and catalytic pyrolysis experiments on cellulosic materials were performed as a model system for the sugar-derived molecules in the aqueous phase. Lignin pyrolysis was not included in the study, because technical lignins like Kraft and Organosolve do not resemble native lignin enough, as these technical lignins, which are isolated after a biomass pretreatment process, widely vary in terms of chemical composition, molecular structure, molecular weight and thus in physical properties, such as solubility and hydrophobicity/hydrophilicity [31]. As a result it will be very difficult, if not impossible, to interpret their pyrolysis results in the framework of this study. For the interpretation of the results it has been assumed that the OPO and APO collected as liquids in the condensers are also present under reaction conditions in the reactor, being present then as vapors or aerosols. This is considered a sound assumption as it has been shown that in our condensers reactions are hardly proceeding [23]. Obviously, it is also assumed that the gases, vapors and aerosols (vapors and aerosols are called for convenience vapors as of now) are the phases reacting with the heterogeneous catalysts, not the solid biomass. We compared our results with continuous oil-producing set-ups. Small-scale systems such as micro-scale CFP (Py-GC/ MS) do not generate the liquid bio-oil product and may not properly reflect similar catalytic effects as in larger scale set-ups due to discrepancy in residence time and partial pressure [32].

2. Experimental

2.1. Feedstock and catalysts

Pyrolysis experiments were conducted using Finnish pine wood sawdust and cellulosic materials as feedstock. For ex-situ modus experiments, the particle size of pine sawdust was in the range of 0.5–2 mm, while for in-situ modus experiments, the pine sawdust was milled down to 250–350 μm. Commercial cotton wool (Caroli®, Medi-Inn) and Avicel cellulose (Sigma-Aldrich) were selected as model compounds for cellulosic materials with high and low molecular weight, respectively.

Two different catalysts were utilized in the test: ZSM-5 and Na_2O/γ-Al_2O_3. The zeolite had a microporous surface of 108 m^2/g and a Si/Al ratio in weight of ~3 (high number of acid sites). The Na content in the Na_2O/γ-Al_2O_3 catalyst was 9.5 wt.%. Both catalysts were delivered as a powder with particles in the range 80–120 μm. Before the experiments, the catalysts were first sieved on a Retsch vacuum filter in order to discard fine particles smaller than 80 μm. Afterwards, they were dried and calcined in an oven at 500 °C overnight.

2.2. Experimental set-up and procedure

Experiments were conducted in a bench scale system equipped with a fluidized bed reactor and a downer reactor (Fig. 1). Experiments were carried out in two different configurations, viz. ex-situ and in-situ modi. The difference between these two modi was the contact pattern of biomass and catalyst. In ex-situ modus, pyrolysis and catalytic upgrading took place in two different reactors, while in the in-situ approach both pyrolysis and upgrading took place simultaneously in the downer reactor. This change of configuration mainly affects the residence time of the pyrolysis vapours before contacting the catalyst.

In the ex-situ modus, biomass was fed to a fluidized sand bed heated through an external furnace at the constant temperature of 500 °C. Constructing details for this unit can be found in previous publications of the group [33]. For each experiment, 1.2 kg of sand was loaded inside the bed, which was fluidized using a constant flow of N_2 (2.0 N L/min). Biomass was fed at a rate of ~1.5 g/min. The vapours produced from the fluidized bed were then conveyed to the top of a downer reactor, constituted by a vertical tube of 1.5 m length and 8 mm internal diameter. At the top of the downer reactor, a screw conveyor was utilized to continuously supply the catalyst. The rotation speed of the conveyor which allowed selecting the required mass flow rate of the catalyst. The screw conveyor, as well as all the tubing in the set-up, were heat traced at the constant temperature of 500 °C. At the bottom of the downer, a cyclone was utilized to separate the catalyst from the vapours, followed by an online filter, able to remove the remaining particles. Then, vapours and aerosols were condensed inside a water-cooled electrostatic precipitator (ESP), operated at 25 °C. An additional intensive cooler operated at −5 °C was installed, to allow the condensation of the remaining vapours. Permanent gases were then filtrated and their volumetric flow was measured with a gas meter. A septum was installed for gas sampling. In this mode, when no catalyst was added to the system, the biomass particles were fed into the fluidized bed pyrolysis, and the vapors were subsequently fed into the empty downer.

For the in-situ modus, the whole experimental system remained the same, except for the fluidized bed and the tubing connecting it to the downer. Those latter units were replaced by a second screw conveyor to feed the biomass particles, placed opposite to the catalyst screw conveyor, at the top of the downer. In the in-situ mode, when no catalyst was added to the system, only the biomass particles were fed at the top of the downer.

In both configurations, different catalyst to biomass ratios were studied. These values are summarized in Table 1. For the zeolite, a range of catalyst/biomass from 0 to 11.7 was studied, while for Na_2O/γ-Al_2O_3, it varied from 0 to 8.2.

Before an experimental run, the system was allowed reaching the desired temperature under constant flow of N_2 (2.0 N L/min). Then, the catalyst and biomass conveyors were started. A typical biomass flow rate was 1.5 g/min, while the rate of the catalyst was changed between 1 and 10 g/min. When the run was concluded, both biomass and catalyst conveyors were stopped, but N_2 was kept flowing for at least 10 min, in order to flush the residual vapors from the system, until the measured outlet gas flow rate was back to the initial values. All the heat tracing was then stopped, the outlet was closed and the system was allowed cooling overnight. One of the experiments was repeated three times under the same conditions to check reproducibility. We assumed for all the experiments the same error.

2.3. Products collection and analysis

The solids collected in the cyclone and in the filter (spent catalyst in the case of ex-situ modus, catalyst and char for in-situ modus) were weighed and sampled. For the ex-situ experiments, the content of the fluidized bed was taken out by means of a vacuum cleaner. The weight of char was obtained by difference, subtracting the weight of the sand. The volume of produced pyrolysis gas was obtained by subtracting the total volume of N_2 flown during the experiments from the total volume of gas measured. The collected gas samples were analysed by means of a micro-GC (Agilent CP900). Ex-situ coke was measured by weight difference between the fresh and used catalyst. in in-situ modus, it was not possible to distinguish between coke and char yields. However, to facilitate the comparison with the data obtained with the other configuration, we assumed that the amount of char produced in all the experiments in in-situ mode was the same as the one obtained in the in-situ experiment without catalyst (when the coke yield was 0).

The amount of liquid products was determined by weighing the collection vessel of the ESP before and after reaction. The residual amounts of oil on the walls of the ESP unit were washed with acetone. The solvent was then evaporated in a rotary evaporator and added to

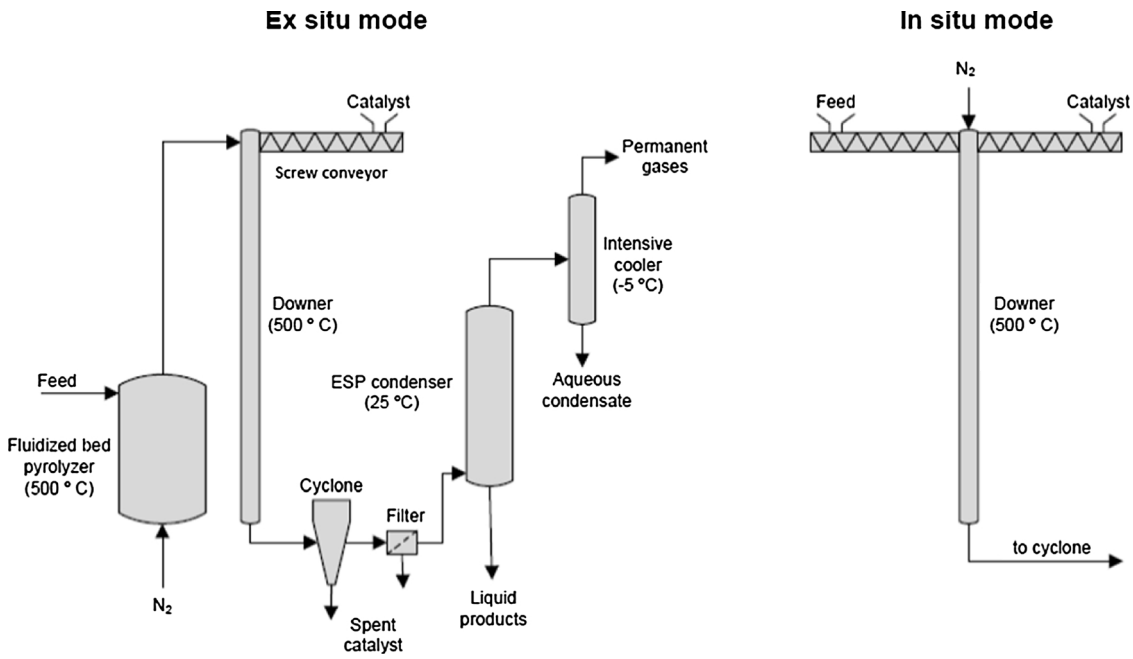

Fig. 1. Schematic representation of the experimental setup for the catalytic pyrolysis experiments. For the in-situ modus, the figure represents only the reactor part, since the whole separation system is the same as for the ex-situ modus.

the liquid collected in the collection vessel. Both aqueous and oil phases were characterized by means of several techniques. The elemental composition, in terms of carbon, nitrogen and hydrogen, was determined by means of an elemental analyser (Inter Science Flash 2000). Oxygen content was obtained by difference. Water content of each phase was determined by means of Karl-Fischer titration (MetroOhm Titrino) and it was utilized to correct the results from the elemental analyser, in order to obtain the elemental composition on dry basis. The molecular weight distribution was measured through gel permeation chromatography (GPC), by means of an Agilent Technologies 1200 system equipped with a refractive index detector (RID), using tetrahydrofuran as an eluent. Standard heteronuclear single quantum coherence nuclear magnetic resonance (HSQC-2D-NMR) was conducted with an Agilent Technologies 400/54 Premium shielded spectrometer. Spectra were processed using MestReNova 9.0 software.

Table 1
Product yields of the thermal and catalytic pyrolysis experiments.

Feedstock	Catalyst	Modus	Catalyst/biomass [kg/kg]	Product yields [% on mass basis, dry ash free intake]						
				Gas[a]	Organics		Water	Char	Coke	Total
					Oil phase (OPO)	Aqueous phase (APO)				
Pine	Zeolite	Ex-situ	0.0	21.7 [2.1]	16.8	29.6	13.7	11.3	0.0	93.0
			1.9	24.5 [3.0]	14.6	17.1	18.0	12.6	2.2	88.9
			3.3	24.7 [2.3]	14.0	15.7	26.8	12.7	4.3	98.2
			4.1	27.2 [2.6]	15.1	12.0	27.2	13.1	4.3	98.9
			4.9	23.8 [2.7]	13.2	14.0	28.4	12.2	5.4	96.9
			7.7	24.0 [2.3]	14.3	8.1	24.7	12.7	5.4	89.1
			11.7	26.7 [5.1]	14.3	5.7	24.4	12.7	8.6	92.4
	Na_2O/γ-Al_2O_3	Ex-situ	0.0	21.7 [2.1]	16.8	29.6	13.7	11.3	0.0	93.0
			0.8	28.3 [1.1]	13.4	5.1	22.4	12.3	4.3	85.7
			1.9	31.2 [1.6]	12.7	2.5	20.2	12.3	7.5	86.3
			3.9	31.6 [1.6]	11.3	2.0	18.9	12.5	15.1	91.4
			7.1	34.8 [1.2]	6.1	1.5	19.9	12.5	19.4	94.2
			8.2	34.3 [1.0]	5.1	1.4	22.3	12.0	24.7	99.8
		In-situ	0.0	18.5 [2.2]	18.4	33.0	11.2	11.5	0.0	92.6
			1.4	26.8 [1.0]	12.9	5.0	15.4	11.5	25.9	97.5
			2.9	34.3 [0.8]	8.7	2.7	19.7	11.5	21.5	98.4
			3.9	35.5 [0.9]	6.7	2.2	21.0	11.5	23.6	100.5
			4.7	34.9 [0.8]	8.4	1.1	16.9	11.5	24.9	97.7
Cotton wool	N/A	Thermal	0.0	30.6 [2.0]	6.8	27.9	23.0	0.7	0.0	89.0
	Zeolite	Ex-situ	5.4	35.7 [2.0]	5.8	7.1	24.8	0.5	10.0	83.9
	Na_2O/γ-Al_2O_3	Ex-situ	5.6	41.1 [1.3]	5.3	2.7	32.3	0.2	14.0	95.5
Avicel	Zeolite	Thermal	0.0	14.6 [2.1]	0.0	51.2	24.8	1.3	0.0	91.8
		Ex-situ	4.2	24.1 [2.7]	0.0	33.0	35.0	1.3	5.0	98.4
		Ex-situ	9.9	22.0 [3.1]	0.0	31.0	31.0	0.6	8.1	92.7

[a] The values in brackets correspond to the CO/CO_2 molar ratios.

2.4. Phase separation of thermal oils

In order to provide a comparison for the production of pyrolysis oil, the oil produced without the catalyst (i.e. the "thermal" oil) underwent phase separation by addition of water. The thermal oil was mixed with distilled water in a plastic tube, to bring the total amount of water in the resulting solution to 60%. Westerhof et al. [21] documented that phase separation already occurs when the total amount of water in the system overcomes 30%. When the total amount of water in the system is higher than 50%, the amount of oil phase is essentially constant and does not vary anymore with further addition of water. The tube was then shaken and the two phases were separated in a centrifuge for 10 min. at 9000 rpm. The resulting phases were then weighed and analysed. For all the subsequent analyses, the amount of water added for the precipitation was deducted from the obtained aqueous phase and the elemental composition was corrected accordingly.

3. Results

In the present study, we have compared the behavior of two different catalysts in a downer reactor, a microporous acidic zeolite (ZSM-5), and a mesoporous basic catalyst (Na_2O/γ-Al_2O_3), in the catalytic pyrolysis of pine wood and cellulosic materials. Although, in the last years much research has been focused on developing new catalyst formulations, mostly regarding chemicals production, [29,30] we have chosen commercially-available catalysts as optimizing and scaling up those new catalyst formulations will still take time. Both catalysts had a similar BET surface area, 122 and 137 m^2/g, respectively and similar particle size (80–120 μm).

For the Na_2O/γ-Al_2O_3 catalyst, two different contacting modes were tested, viz. in-situ and ex-situ, to analyze if a different contact pattern between the catalyst and the vapors affects the yield and quality of the products. In in-situ modus, both biomass and catalyst were fed together in a downer reactor, while in ex-situ modus, pyrolysis vapors were produced in a fluidized bed and subsequently catalytically upgraded in a downer reactor. In-situ experiments used biomass of a smaller particle size and were aiming at improvement of the oil phase yield and deoxygenation level. It has been reported that smaller particles result in less char and gas, and thus, more liquid products. [28] The residence time of vapors before contacting the catalyst was much less in the in-situ modus as compared to the ex-situ modus (0.5 vs. 1.8 s). This defines the main difference between the two operation methods; specifically, the degree of thermal cracking that the vapors undergo before contacting the catalyst. In the in-situ modus, the catalyst is in contact with primary vapors, while in the ex-situ modus the vapors are already thermally cracked when contacting the catalyst [3,34].

For both catalysts, different catalyst-to-biomass ratios were evaluated. Table 1 summarizes the measured product yields (mass basis) for all the pyrolysis experiments. The liquid fraction was split in an aqueous phase (APO) and the desired oil phase (OPO). This separation occurred naturally in the case of the catalytic oils, due to an increased formation of water, [5,24] and by the addition of water in the thermal oils (more details on this phase separation can be found in the Experimental Section). The OPO and APO yields obtained after phase separation by water addition in the thermal pyrolysis experiment are used for comparison with the catalytic OPO and APO.

The yield, on carbon basis, and oxygen content of OPO and APO are shown in Fig. 2. Mass balance closure was between 84 and 100% in all the experiments, what can be consireded as acceptable due to the complexity of this type of systems. Experiments with the lowest mass balance closure did not influence the overall trends. There was no correlation between any of the individual yields and the mass balance clouse. Besides, an acceptable coefficient of variation (< 10%) for the product yields was obtained, based on 3 repeated identical experiments. Also, for reproducibility purposes, elemental analysis of the APO and OPO samples was performed three times on each sample (error bars available in the graphs). In the sections below, OPO and APO yields will be discussed on carbon basis while for char, coke, gas and water the mass basis will be used.

In all the cases of pine wood, the maximum OPO yield was obtained

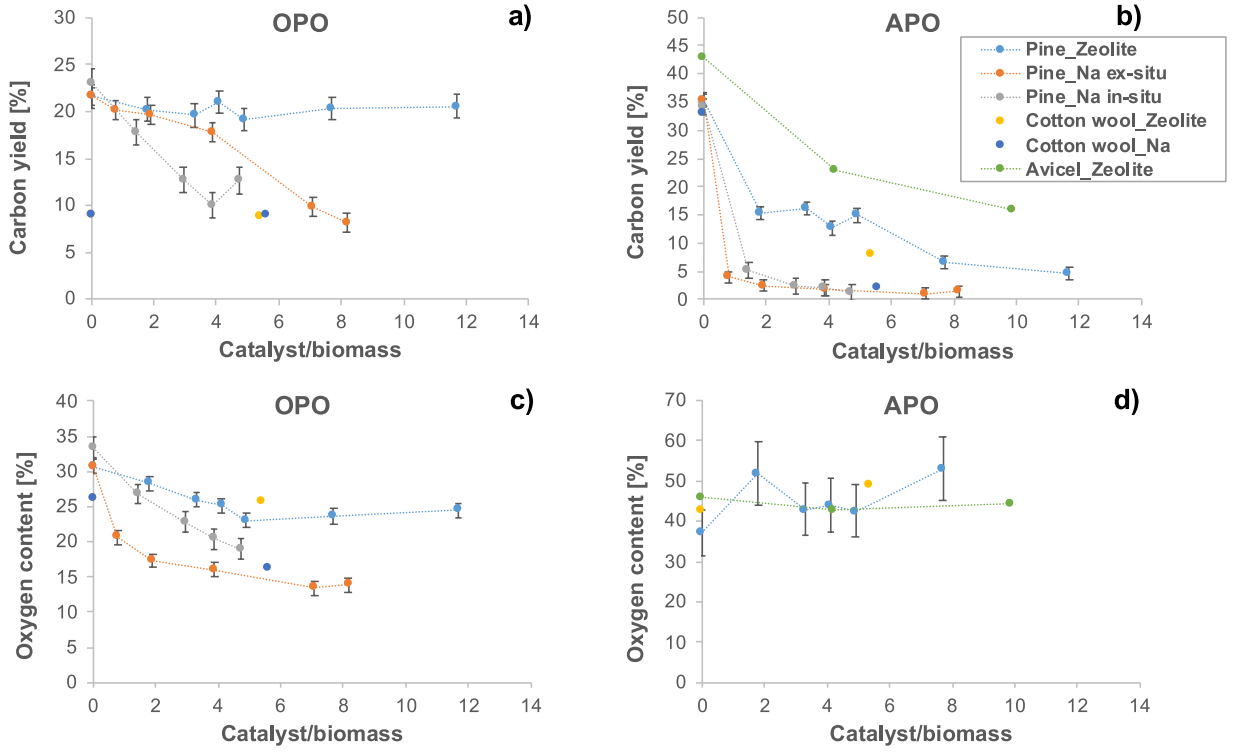

Fig. 2. Carbon yield and oxygen contents in organics fraction: a) Carbon yield in oil phase organics; b) Carbon yield in aqueous phase organics; c) Oxygen content in oil phase organics; d) Oxygen content in aqueous phase organics.

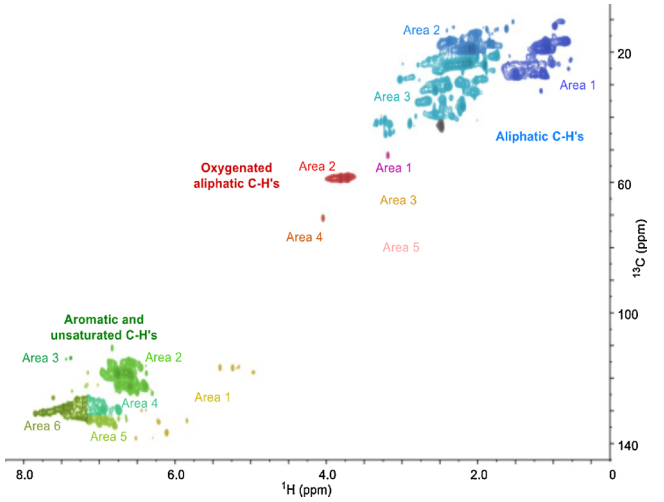

Fig. 3. 2D-NMR spectrum of the oil phase of the pine pyrolysis oil obtained in *ex-situ* mode, with zeolite as catalyst (catalyst/biomass = 11.7). Aliphatic C–H region (blue); Area 1: alkanes, Area 2: Ar-Me, Area 3: Allylic/benzylic. Oxygenated aliphatic C–H region (red); Area 1: OMe, Area 2: Ar-OMe, Area 3: ROH, Area 4: RO, Area 5: levoglucosan. Aromatic and unsaturated C–H region (green); Area 1: alkenes, Area 2: guaiacolics, Area 3: Phenanthrolines, Area 4: phenolics, Area 5: aromatics, Area 6: polycyclics. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

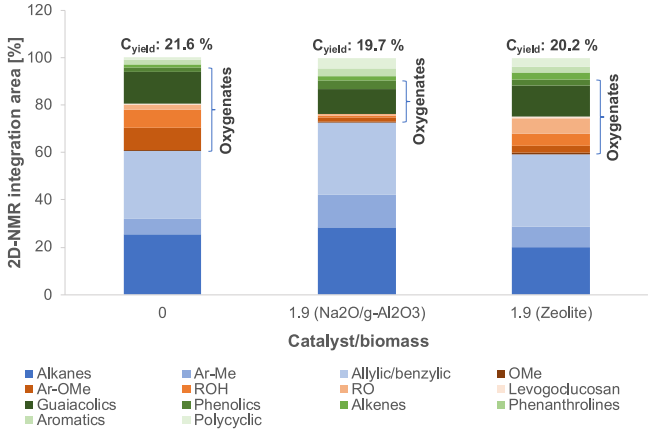

Fig. 4. 2D-NMR areas integration [%] of the oil phase of pine pyrolysis oils: thermal ex-situ oil; zeolite ex-situ oil and $Na_2O/\gamma\text{-}Al_2O_3$ catalyst ex-situ oil (catalyst/biomass = 1.9).

in the thermal pyrolysis experiments, reaching a maximum 23%. This is in agreement with the values reported in literature for continuous oil producing set-ups, including commercial large-scale plants, like the one from KIOR technology (~ 17%). [1,4,5,11,12,15]

The most general observation was that for both catalysts and operating modi, the total yield of liquid organics (OPO + APO) decreased when increasing the catalyst to biomass ratio in favor of gas, water and coke. The yield of aqueous phase organics (APO) was strongly reduced when increasing the catalyst to biomass ratio. At constant catalyst to biomass ratio, the $Na_2O/\gamma\text{-}Al_2O_3$ catalyst had the highest reactivity for this reaction. Despite the difficulty in the measurement of the oxygen content of APO due to the high amount of water present, it could be observed that, the oxygen content of these organics was hardly affected by the catalysts and it did not decrease relative to the thermal APO. Although it is probable that the catalyst could deoxygenate to some extent the organics in the aqueous phase, and the deoxygenated product moved from the APO to the OPO due to its decrease in polarity, from an overall point of view, this was not observed. Hence, overall, this product was not deoxygenated. A clear difference between the catalysts was the yield of OPO; while the zeolite kept a constant yield (~ 20%), the alkaline catalyst reduced the yield down to below 10%. The oil yield obtained with ZSM-5 is comparable with other studies reported in literature that used the same catalyst (14–26%). [3,5] It is worth mentioning that our results are being compared with continuous oil-producing set-ups. Small-scale systems such as micro-scale CFP (Py-GC/MS) do not generate the liquid bio-oil product and may not properly reflect similar catalytic effects as in larger scale set-ups due to discrepancy in residence time and partial pressure [32].

Babich et al. [35] used Na_2CO_3 to catalyze the pyrolysis of chlorella algae, and also observed that, in the presence of the Na catalyst, the solid and gas yield increased and bio-oil yield decreased, when compared with noncatalytic pyrolysis under the same conditions.

Using the $Na_2O/\gamma\text{-}Al_2O_3$ catalyst resulted in a significantly lower oxygen content of the OPO as compared to the zeolite. With the zeolite the lowest value measured was 23%, whereas for $Na_2O/\gamma\text{-}Al_2O_3$ ~13% was reached. Nguyen et al. [36] also observed a high deoxygenation activity of $Na_2O/\gamma\text{-}Al_2O_3$ catalyst in the catalytic pyrolysis of pine, reducing the oxygen content from 42% in the thermal bio-oil, to 12% in the catalytic oil.

OPO samples were further characterized by 2D-NMR, which provides a detailed overview of the chemical functionalities in the bio-oils, without restrictions of MW. [26,37–40] As an example, Fig. 3 shows the 2D-NMR spectrum for the pine OPO produced in ex-situ modus with zeolite as catalyst. Peaks and regions of the spectra corresponding to specific functional groups were identified and labelled, according to the methods reported in the literature. [39,41] Three regions were identified in all the cases: the non-oxygenated aliphatic C–H region, the oxygenated aliphatic C–H region, and the aromatic and unsaturated C–H region. Some specific functional groups were identified within those regions. The integration of those groups for selected OPO samples is shown in Fig. 4. NMR results confirmed the elemental analysis, showing that OPO produced using $Na_2O/\gamma\text{-}Al_2O_3$ was more deoxygenated. Most of the aliphatic R—OH, R—O and methoxyl groups disappeared during catalytic pyrolysis, while the formation of aliphatic C—H groups was favored, especially with the $Na_2O/\gamma\text{-}Al_2O_3$ catalyst (~73%). In the aromatic region, it can be observed that guaiacolic groups are the dominant area in the thermal oil, likely produced from the cleavage of lignin compounds and their condensation, while in the catalytic oils, the guaiacolics region is reduced (mostly with $Na_2O/\gamma\text{-}Al_2O_3$) in favor of phenolics, aromatics and polycyclic compounds.

No differences were observed in the H/C molar ratio (on average 1.2) of OPO between the catalysts, the catalyst/biomass ratios and the contacting modi. Regarding water formation, an increase in the water yield was observed in all the catalytic experiments, in comparison to the thermal ones. When comparing the two catalysts, zeolite produced slightly more water. The water content of OPO was on average 11% and 5%, for zeolite and $Na_2O/\gamma\text{-}Al_2O_3$ catalyst, respectively. Coke on catalyst and to lesser extent gas formation was clearly more pronounced with the $Na_2O/\gamma\text{-}Al_2O_3$ catalyst. The molar CO/CO_2 ratios are also reported in Table 1 (number between brackets in the gas column). It was observed that the $Na_2O/\gamma\text{-}Al_2O_3$ catalyst gave lower values of the CO/CO_2 ratio in comparison to the zeolite.

Another indicator of the oil quality improvement during catalytic pyrolysis is the reduction of the mass molecular weight (MMW) of the sample. Fig. 5a shows the comparison of MMW distribution of OPO of thermal and ex-situ catalytic experiments. In all the tests, the catalytic oil had a lower MMW in comparison to the thermal oil: the former had an average MMW around 700 Da, while the latter was usually around 300 Da. In Fig. 5b it can be observed that an important fraction of the thermal OPO with a MMW above 500 Da disappeared in favor of smaller fractions. $Na_2O/\gamma\text{-}Al_2O_3$ catalyst was always more active in reducing the MMW of the oil than the zeolite.

Table 1 and Fig. 2 also show the results of the comparison of the thermal and catalytic pyrolysis experiments with two types of cellulose (cotton wool and Avicel cellulose) and for both catalysts, in ex-situ

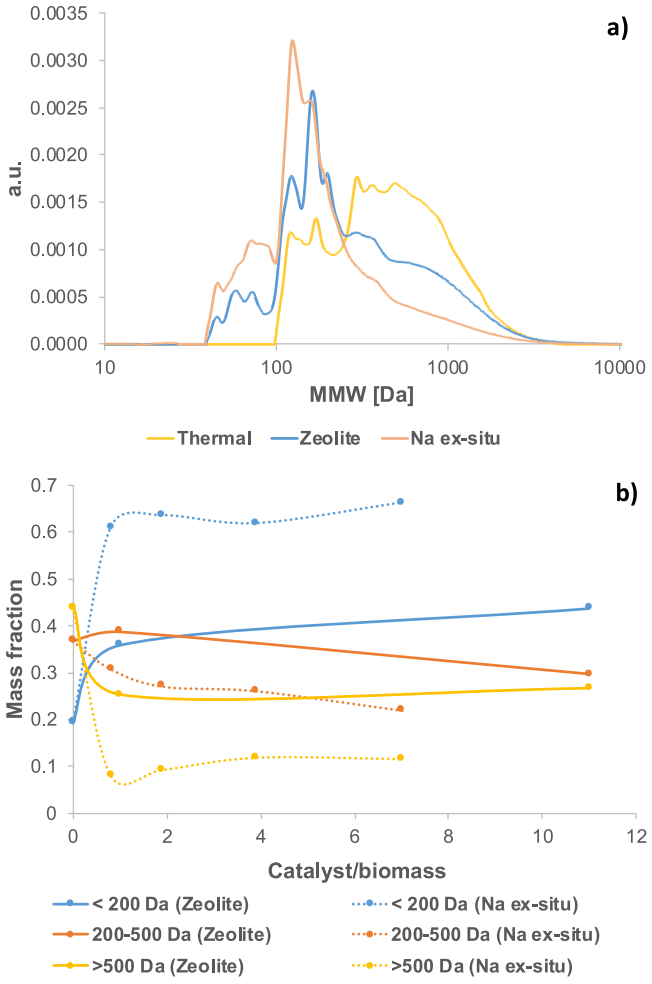

Fig. 5. a) Comparison of molecular weight distribution of the oil phases produced thermally and catalytically in ex-situ modus. b) Molecular weight fractions of the oil phases produced thermally and catalytically in ex-situ modus, as a function of the catalyst to biomass ratio.

mode. Compared to pine wood, the experiments with cellulose were characterized by a very low char formation and higher liquid organic yields (APO + OPO). However, the OPO yields were definitely lower than for pine wood. Interestingly, this yield strongly depended on the kind of cellulose tested. With Avicel cellulose, no OPO was formed. Cotton wool did produce some OPO which did not (hardly) decrease upon addition of the catalysts. The OPO was deoxygenated with Na_2O/γ-Al_2O_3. Like for pine, the APO yield decreased strongly in the presence of the catalysts.

It might have been the case that in the downer (in-situ modus) higher char yields were obtained due to lower heat transfer rates as compared to the sand fluidized bed used for the ex-situ experiments. This was investigated by the comparison of the in-situ char yield with the ex-situ char yield for runs with no catalyst addition (catalyst-to-biomass = 0). In both cases the char yield was ca. 11.5% showing that also in the downer the heat transfer rate is high. Comparing the two contacting modi at catalyst-to-biomass ratios below 5, it is evident that coke production was quite higher in the in-situ modus, while OPO yield was hardly affected. It can be then seen that coke production insitu modus was always around 23% regardless the catalyst-to-biomass ratio. This may be due to the higher reactivity of the primary vapors. Kalogianis et al. observed a different trend insitu modus, with an increase in the coke yield with the catalyst/biomass ratio. [42] In the corresponding ex-situ experiments, coke increased from 4 to 25% with increasing the catalyst-to-biomass ratio from 0.8 to 8. It was observed that Na_2O/γ-Al_2O_3 catalyst is more prone to the production of coke than the zeolite, reaching values of almost 25% when used in both ex-situ and in-situ modi. These results agree with previous literature [42], where the authors also obtained high coke yields of up to 52% (in carbon basis) with a basic catalyst (MgO).

4. Discussion

The operating modus was changed from ex-situ to in-situ, in combination with feeding smaller particles, aiming at improving the yield of OPO, being the target product. It turned out, as expected from reported data, [28] that the thermal OPO yield increased, though slightly, due to the smaller particles used. However, comparing the two contacting modi it became evident that coke production was higher in the in-situ modus, while the OPO yield was lower. At a catalyst to biomass ratio of 3.9, coke yields were 25 and 15% and OPO yields 10 and 20%, respectively, for in-situ and ex-situ modi.

Also, the fact that the in-situ mode produced an oil with a lower degree of deoxygenation indicates a higher propensity to catalyst deactivation in the in-situ mode. [3] These findings can be ascribed to the reactivity of the OPO vapors. In the ex-situ modus the vapors are at 500 C for ~2 s before contacting the catalyst, whereas for in-situ operation this is just ~0.5 s. Following this line of reasoning, the primary, oxygen richer vapors, which come in contact with the catalyst are more prone to form coke than the more (thermally) cracked vapors. Based on these results and reported OPO yields, with 26% as maximum value, [3,5] obtained in different reactor systems (with in-situ and ex-situ contacting modi), we argue that considerably higher OPO yields of catalytic pyrolysis are not expected to be achieved by process improvements. These results obtained in laboratory-scale are also in fully agreement with large-scale processing technologies (e.g. the carbon yield in KIOR commercial-scale technology was ~17%) [1].

Assuming that the catalyst does not interfere in the primary pyrolysis reactions going on inside the pyrolyzing particle, and that one of the main functionalities of the typical catalysts is cracking, it could be reasoned that the maximum yield of liquid organics (OPO + APO) of catalytic pyrolysis is determined by the thermal pyrolysis process. This was confirmed experimentally.

When comparing both catalysts, the results on oil characterization (analysis elemental, 2D-NMR and GPC) showed that Na_2O/γ-Al_2O_3 catalyst was always more active in deoxygenating and reducing the MMW of the oil than the zeolite. The latter may be related to the limitation of the zeolite catalyst to convert some of the larger molecules produced during pyrolysis due to its smaller pore size. [2,43,44] Also, from the lower values of the CO/CO_2 ratios obtained with Na_2O/γ-Al_2O_3 catalyst, in comparison to the zeolite, it can be concluded that Na_2O/γ-Al_2O_3 catalyst favors the reactions leading to CO_2 formation, such as decarboxylation and ketonization. Conversely, zeolite fosters the dehydration reaction, as it was also observed from the higher water yield obtained, in comparison to the experiments with Na_2O/γ-Al_2O_3 catalyst. These results are in agreement with previous literature, where it has been shown that basic catalysts favor condensation, ketonization and decarboxylation reactions, while acid zeolite materials promote cracking, alkylation, aromatization, isomerization, dehydration and decarbonylation reactions. [2,11,42,45–47] In a recent study, in a pilot-scale study on catalytic pyrolysis of biomass using basic catalysts (MgO), K.G. Kalogiannis et al. also observed that deoxygenation was mostly achieved through carbon coupling reactions, which resulted in increased CO_2 yields compared to the acidic ZSM-5 catalyst, while CO and H_2O yields decreased. This led to an increased hydrogen recovery (and thus, improve fuel properties) in the produced bio-oils. [42]

In the following an overall lumped reaction path scheme for catalytic APO and OPO conversion is proposed. It is not intended to provide mechanistic insights; it is merely a description of the experimentally observed mass balance. It does, however, give directions on desired chemical paths for enhancing the OPO yield (see later).

For APO the following reaction is proposed:

$$(CH_xO_y)_m \rightarrow Gas + Coke + H_2O \quad (1)$$

The rational behind this reaction is that the oxygen content and MMW of the collected APO was not affected by the catalyst to biomass ratio. This means that a thermally produced APO molecule can either catalytically react to gas, coke and water or does not react. This reaction was observed experimentally for pine wood APO. In order to confirm the hypothesis that APO is primarily composed out of sugars and that it reacts according to Reaction 1, experiments with cellulosic materials were ran. The data support that sugars give primarily APO as, depending on the molecular weight of the cellulose, no to hardly OPO was produced during (catalytic) pyrolysis. With Avicel cellulose, no oil phase was formed, probably due to the lower polymerization degree of this type of cellulose (around 300, against ca. 10,000 or more of cotton wool). [48] With both cellulosic materials, upon adding the catalysts, the APO yield decreased at the same rate as pine APO.

For OPO, the following reaction is proposed:

$$(CH_xO_y)_m \rightarrow (CH_aO_b)_n + Gas + Coke + H_2O \quad (2)$$

with: $a < x$, $b < y$, $n < m$

This reaction is substantiated by observations that upon increasing the catalyst to biomass ratio, the OPO phase becomes deoxygenated and cracked, to an extent depending on the catalyst-to-biomass ratio used. After the APO fraction reduced to nearly zero, the catalytic pyrolysis of pine wood still resulted in a further increase of the gas, coke and water yield, which justifies these products as reaction products from OPO (most clearly seen in the $Na_2O/\gamma\text{-}Al_2O_3$ ex-situ series). There is no evidence for the (overall) conversion of APO in OPO or vice versa, because their yields did not show opposing trends. Some of the organic compounds in APO may migrate to the OPO, due to changes in the compounds polarity after the different chemical routes taking place, such as aromatization and aldol-condensation. [49] However, in overall terms, this migration of compounds from APO to OPO is not translated into an increased OPO yield.

Globally, the proposed reaction path model is in agreement with one of the hypothesis of R.H. Venderbosch, [1] which stated, that “catalytic pyrolysis appears to favor the production of deoxygenated products from the lignin fraction only, whereas carbohydrates are converted to coke, gas and water”.

In Fig. 6 the carbon yield and oxygen content of OPO are plotted to illustrate the catalytic pyrolysis process. By adding a small amount of catalyst, already enough extra water is produced to split the single-phase oil into OPO and APO. The original 60% yield of oil is then split into 35% APO and 25% OPO. With the current catalysts, this 35% APO is not used for OPO production. The product yield of catalytic pyrolysis is thus limited to the yield of OPO obtained in thermal pyrolysis, being only ~25%, which is a critical barrier to develop a competitive technology. Using the typical catalysts some desired characteristics of the product were achieved: lower oxygen, lower water content and low MMW. Again, all these properties were achieved at the expense of the OPO yield. The loss in OPO carbon yield operating in ex-situ modus is more evident when reducing the oxygen content below 20%.

Fig. 7 shows a comparison of the yield and oxygen content of OPO in this study with data previously reported in laboratory-, bench- and pilot-scale studies. These other studies include different reactors, commercially available catalysts, in-situ or ex-situ operation, catalyst to biomass ratio and feedstocks [3,5,17,20,42]. From this figure, it can be seen that the included OPO yield of catalytic pyrolysis do not or only hardly exceed the OPO yield of thermal pyrolysis. The resembles with our data supports our conclusions further. None of the data sets shows catalytic activity towards OPO yields higher than the thermal OPO yield. In fact, the individual data sets show the undesired coupling of an decreasing yield with lower oxygen contents.

For higher OPO yields, catalysts being able to convert the sugar fraction (APO) into OPO are required. These catalysts should, amongst other functionalities, oligomerize APO to OPO instead of cracking it to gas and charring it.

For fuel purposes, catalytic pyrolysis must be compared to thermal pyrolysis followed by hydrodeoxygenation (HDO), or catalytic pyrolysis in an H_2 atmosphere. [47,50–52] HDO is able to transform the light oxygenates (APO) into oil-soluble compounds (OPO) [51]. In fact, with thermal pyrolysis followed by HDO, yields up to 47% on carbon basis can be achieved [1,53]. Despite additional costs for the hydrotreater and H_2 supply, hydrotreating may be more competitive than catalytic pyrolysis, at least at the current state of the art.

5. Conclusions

Catalytic pyrolysis is studied by following two families of organic compounds in the produced liquid, viz. oil phase organics (OPO) and aqueous phase organics (APO). These two classes of compounds can be

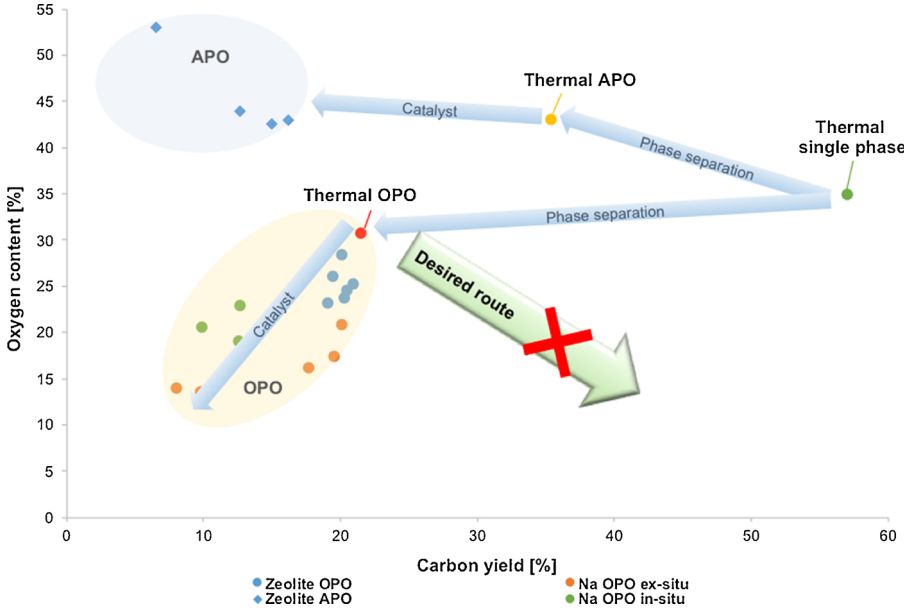

Fig. 6. Oxygen content (water free basis) and carbon yield of the thermal (single and separated APO and OPO) and catalytic oils (APO and OPO).

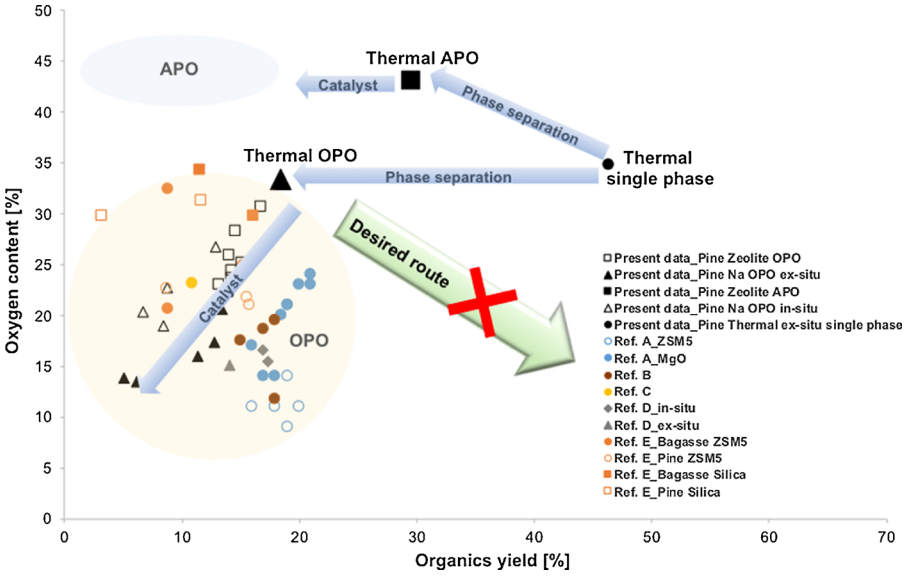

Fig. 7. Comparison of the data obtained in this study with previous studies from the literature, on the organics yield and oxygen content (water free basis) in the catalytic pyrolysis of biomass under different conditions. **Ref. A:** Beechwood, Circulating Fluid Bed (CFB) system (pilot-scale, 1 kg/h), MgO and ZSM5 as catalysts, in-situ modus [42]; **Ref. B:** Beechwood, CFB system (pilot-scale, 1 kg/h), HZSM5 as catalyst, in-situ modus [5]; **Ref. C:** Pine, Fluidized bed (lab-scale, 450 g/h) and CFB system (pilot-scale, 1 Tn/day), γ-Al_2O_3 as catalyst, in-situ modus [20]; **Ref. D:** Pine, Fluidized bed (bench-scale, 150 g/h), HZSM5 as catalyst, in-situ and ex-situ modi [3]; **Ref. E:** Pine and bagasse, CFB system (pilot-scale, 1 kg/h), ZSM-5 as catalyst, in-situ modus [17]. We have used the terminology of the original papers regarding lab- and pilot-scale.

also identified in thermal bio-oil through water precipitation and arise naturally in the catalytic process, due to phase separation caused by the higher amount of produced water. OPO represent the desired product for energy purposes such as fuel oil or refinery feed. OPO compounds are mostly, but not exclusively, derived from lignin.

Regardless the process conditions, for all the analyzed catalysts, feedstocks and process configurations (in-situ vs. ex-situ) tested, the OPO yield never exceeded the amount of OPO produced under thermal conditions. The amount of thermal OPO can be therefore considered as the maximum yield of product from catalytic pyrolysis for fuel applications.

Both analyzed catalysts (zeolite and Na_2O/γ-Al_2O_3) were very active in converting APO, even at very small catalyst-to-biomass ratios. Their conversion did not result in any increase in OPO, but strongly contributed to coke and water. The oxygenated organic compounds were thus lost, in view of OPO production. Thus, is it possible to increase the oil yield of catalytic pyrolysis? The answer is no when using commercially catalysts or slighty modified versions of those. A path towards substantially higher OPO yields from catalytic pyrolysis requires the conversion of APO into OPO. This may be achieved by new catalysts that oligomerize APO into OPO.

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